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Infrared Spectra of Molecules and Materials of Astrophysical Interest

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SUMMARY OF PROGRESS

We have been studying the vibrational spectra from 4000 to 33 cm^{-1} of several molecules which may be present in the atmosphere of the Jovian planets. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the compositions of the cloud covers of several of the planets; (2) provide structural information under favorable circumstances; (3) provide necessary data from which accurate thermodynamic data can be calculated; (4) and furnish information as to the nature of the potential energy function of the molecules and forces acting within them.

Gerard P. Kuiper[1] has pointed out that the Jovian atmospheres are expected to contain H_2, He, N_2, H_2O, NH_3, CH_4, Ar and possibly SiH_4. He has also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below 120°C [see Table 8, pg. 349-350 of reference (1)]. He has also pointed out that until more is known about the atmospheres of the planets it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work.

Some of the molecules which we have studied can be produced photochemically from methane, ammonia, and hydrogen sulfide which are thought to be constituents of the planets with reducing atmospheres. Some of the compounds will polymerize under ultraviolet radiation and drop out of the atmospheres. However, planets with a hot base, like that of Jupiter, may rebuild molecules destroyed photochemically. Therefore, we have used these criteria in selecting the compounds which we have studied. In our initial work on the vibrational spectra of molecules of astrophysical interest we studied hydrazine[2] and methylamine.[3] However, there are several other small molecules which contain hydrogen, carbon and nitrogen which also should be possible constituents of the reducing atmospheres and we previously selected methyl hydrazine[4], unsymmetrical dimethyl hydrazine[5], symmetrical dimethylhydrazine[6], propylene imine[7], and 1-pyrazoline[8] for our studies. A study on HNCS and DNCS has been completed and a copy of the paper as submitted to the journal, Molecular Crystals and Liquid Crystals, can be found in Appendix I.

Closely related to these nitrogen containing compounds has been our work on the carbonyl containing molecules. We have previously reported work on carbon trioxide[9], trifluoromethyl peroxide[10], ethylene carbonate[11], γ-butyrolactone[11], cyclopentanone[11], oxalyl chloride[12], glyoxal[13] and oxalyl bromide[14]. In a continuing study of oxalyl halides, we have completed an investigation of oxalyl fluoride and a copy of the paper as submitted to the Journal of Chemical Physics is presented in Appendix II.

Molecules in the series of halogenated oxalic acids have been the subject of considerable controversy, with respect to the possibility of cis or trans structure, or both.[15-22] Recent work at this laboratory has shown oxalyl chloride[12] and bromide[14] to exist in both isomeric forms in liquid and vapor phases. However, spectra of crystalline samples of these compounds showed complete conversion to the trans form upon solidification. The last reported vibrational study of oxalyl fluoride[20] concluded the molecule exists in only the trans form, and the spectra were interpreted on this basis. Since this compound has not been studied in the crystalline phase, work has been undertaken to determine if the fluoride behaves in a manner comparable to the other oxalyl halides and to observe possible crystalline effects.

The infrared spectra have been obtained for the solid and vapor phases and the Raman spectra for the solid and liquid phases. The results will be presented and shown to be consistent with the presence of two isomers in the fluid states. Also of particular interest was the frequency for the internal torsional oscillation.

The vibrational work on the series of compounds, $(COCl)_2$, $(COBr)_2$, and $(COF)_2$, leaves little doubt that there are two isomeric forms in the gas phase. It is interesting that glyoxal[13] and 2,3-butanedione[23] exhibit only one form which leads one to the conclusion that the halogens provide a stabilizing influence for the cis configuration. This stabilization can be rationalized on the basis of the relative magnitude of the non-bonded forces between the halogens and the carbonyl group. For example, Saegebarth and Wilson[24] found the stable configurations of fluoroacetyl fluoride to be the trans and the unexpected cis configuration. These data clearly demonstrated the stabilizing influence of the fluorine-fluorine interaction. On this basis one then expects the halogen-substituted oxalyl compounds to be the most favorable for the observation of a cis isomer.

Hencher and King's conclusion that oxalyl fluoride exists only in the trans form[20] in all phases demonstrates the importance of taking spectra of the solid phase for the detection of isomers. They used only gaseous infrared and liquid Raman samples to obtain their vibrational data. The contamination of their Raman sample also contributes to the uncertainty of their vibrational assignment. Our solid-phase work clearly demonstrates the structural difference that exists between the rigid and fluid phases of the oxalyl fluoride molecule.

The apparent factor group splitting of the C-C stretching vibration suggests that there are at least two molecules per unit cell. From the mutual exclusion it was concluded that the oxalyl fluoride molecule is centrosymmetric in the crystal and the molecules probably occupy C_i sites. For molecules occupying such sites, packing considerations suggest that the most probable space groups would be D_{2h}^{10}, D_{2h}^{15}, C_{2h}^{5} or C_{2h}^{6} with two or four molecules per unit cell.[25] In view of the crystal space group for other molecules of similar structure either the monoclinic (C_{2h}^{5}) or orthorhombic (D_{2h}^{15}) space groups could be expected to give a close-packed arrangement of molecules retaining C_i symmetry.

A temperature study of the far-infrared spectrum of the solid showed that the 82 cm^{-1} band sharpens drastically with annealing and results from an intermolecular fundamental. The 94 cm^{-1} band was not particularly temperature sensitive so it was concluded that this band was the torsional fundamental which shifted from 54 cm^{-1}. Such a drastic shift with condensation for the torsional oscillation has been found for the glyoxal molecule[13] where the band shifted from 128 cm^{-1} in the gas phase to 192 cm^{-1} in the solid.

Attempts to observe the microwave spectra of glyoxal[26], diacetyl[26], and oxalyl chloride[27] have been unsuccessful. However, the microwave spectrum of oxalyl chloride may be so weak due to quadrupole splitting that its observation would be extremely difficult. Oxalyl fluoride, having only one isotope and no quadrupole moment, should represent a more ideal case; and observation of the microwave spectrum would provide conclusive proof of the existence of a cis isomer. Thermodynamic properties have been calculated and are presented in Table 1.

In an earlier publication[28] we reported the mid infrared spectra of gaseous and solid HNCS and DNCS. The assignment of the out-of-plane skeletal bending mode, ν_6, was stated to be quite uncertain since the only apparent choice gave an extremely high frequency when compared to the similar motions of the HN_3 and HNCO molecules. At the time of our initial investigation, it was not possible for us to obtain the Raman spectrum of this slightly colored material. It was expected that this N=C=S out-of-plane mode might have a reasonable polarizability change and thus be detected in the Raman effect. Therefore, we have investigated the Raman spectra of solid HNCS and DNCS.

Also, in the earlier investigation three definite bands were observed in the spectra of the solids in the vicinity of ν_5, the N-H bending mode. No satisfactory explanation could be given for their origin, although a tentative suggestion of lattice modes was given. We have now investigated the lattice region of the spectrum and evidence has been found for more than one crystalline form. These studies represent a continuation of earlier investigations[29-32] of the frequencies of the lattice vibrations of molecular crystals.

The infrared and Raman spectra of polycrystalline HNCS have been recorded and a vibrational assignment is suggested for the six internal fundamentals. The previously unassigned out-of-plane skeleton bending mode has been tentatively assigned to the band at 682 cm^{-1}. The infrared and Raman counterparts of the C=N stretching fundamental were widely separated which suggests that the crystal structure may be centrosymmetric. Factor group splitting was observed for several of the bands and was most apparent for the N-H bending vibration where four bands were clearly defined. On the basis of the observed factor group splitting for ν_5, it would appear that HNCS has at least four or eight molecules per unit cell depending upon whether or not it has an inversion center. The vibrational data also provides strong evidence for the existence of at least two different crystalline phases, and the vapor-solid frequency shift for ν_1 suggests a relatively short N-H---N distance. Thermodynamic properties have been calculated and are presented in Table 2.

FUTURE WORK (NGR-41-002-003-3)

We are continuing our investigation of the vibrational spectra of small molecules which may be possible constituents of the Jovian atmospheres. The data will be used to calculate thermodynamic properties, force constants and other useful molecular properties when possible. At present work is still continuing on 2,3-butanedione. The vibrational study of azomethane is nearing completion. The results of these studies will be in the next progress report. We have also begun an investigation of oxalyl chloro-fluoride which is a continuation in our study of molecules containing carbonyls. The results of this work should appear in a future report.

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Table I. Thermodynamic Calculations for trans-Oxalyl Fluoride

	S	$-(F-H_0)/T$	$(H-H_0)/T$	Cp
Temperature 273.15° K				
Translational	39.098367	34.130442	4.967925	4.967925
Rotational	24.681008	21.700643	2.980365	2.980755
Vibrational	7.667962	3.167059	4.500903	9.863568
Total	71.447336	58.998144	12.449193	17.812248
Temperature 300.00° K				
Translational	39.564167	34.596241	4.967925	4.967925
Rotational	24.960487	21.980088	2.980400	2.980755
Vibrational	8.633685	3.613170	5.020515	10.737274
Total	73.158338	60.189499	12.968839	18.685954
Temperature 400.00° K				
Translational	40.993350	36.025424	4.967925	4.967925
Rotational	25.817997	22.837508	2.980489	2.980755
Vibrational	12.110209	5.307553	6.802656	13.428474
Total	78.921555	64.170485	14.751069	21.377154
Temperature 500.00° K				
Translational	42.101910	37.133985	4.967925	4.967925
Rotational	26.483133	23.502592	2.980542	2.980755
Vibrational	15.335226	6.995009	8.340217	15.462201
Total	83.920268	67.631585	16.288684	23.410881
Temperature 600.00° K				
Translational	43.007669	38.039744	4.967925	4.967925
Rotational	27.026589	24.046012	2.980577	2.980755
Vibrational	18.298959	8.635555	9.663405	17.029863
Total	88.333217	70.721311	17.611907	24.978543
Temperature 700.00° K				
Translational	43.773479	38.805553	4.967925	4.967925
Rotational	27.486074	24.505472	2.980603	2.980755
Vibrational	21.019479	10.213120	10.806359	18.247644
Total	92.279032	73.524145	18.754887	26.196324
Temperature 800.00° K				
Translational	44.436852	39.468927	4.967925	4.967925
Rotational	27.884099	24.903477	2.980622	2.980755
Vibrational	23.520789	11.722402	11.798386	19.198901
Total	95.841740	76.094806	19.746933	27.147581
Temperature 900.00° K				
Translational	45.021989	40.054064	4.967925	4.967925
Rotational	28.235181	25.254545	2.980637	2.980755
Vibrational	25.827027	13.163157	12.663870	19.947200
Total	99.084198	78.471766	20.612432	27.895880

Table I (Continued)

	S	$-(F-H_0)/T$	$(H-H_0)/T$	Cp
Temperature 1000.00° K				
Translational	45.545413	40.577488	4.967925	4.967925
Rotational	28.549235	25.568587	2.980648	2.980755
Vibrational	27.960586	14.537574	13.423012	20.540998
Total	102.055234	80.683648	21.371585	28.489678

* These calculations were made using the solid phase frequencies and assuming all vibrations to be harmonic. Assuming the following molecular geometry: r(C-C) = 1.50 Å, r(C-F) = 1.35 Å , r(C=O) = 1.18 Å, CCO = 124.0°, and CCF = 111.0°; the moments of inertia I_A = 86.381034, I_B = 139.567223 and I_C = 225.948259 (AMU) Å^2 were calculated and used in these calculations presented.

TABLE II. THERMODYNAMIC CALCULATIONS FOR HNCS

	S	$-(F-H_0)/T$	$(H-H_0)/T$	Cp
Temperature 273.15° K				
Translational	37.713905	32.745980	4.967925	4.967925
Rotational	17.745080	14.764851	2.980229	2.980755
Vibrational	1.610823	0.413314	1.197509	3.687530
Total	57.069808	47.924145	9.145663	11.636210
Temperature 300.00° K				
Translational	38.179704	33.211779	4.967925	4.967925
Rotational	18.024560	15.044284	2.980276	2.980755
Vibrational	1.978319	0.536870	1.441449	4.149779
Total	58.182583	48.792933	9.389650	12.098459
Temperature 400.00° K				
Translational	39.608887	34.640962	4.967925	4.967925
Rotational	18.882070	15.901674	2.980396	2.980755
Vibrational	3.366087	1.071116	2.294971	5.468653
Total	61.857043	51.613751	10.243292	13.417333
Temperature 500.00° K				
Translational	40.717447	35.749522	4.967925	4.967925
Rotational	19.547206	16.566738	2.980468	2.980755
Vibrational	4.689062	1.663961	3.025101	6.374718
Total	64.953714	53.980221	10.973493	14.323398
Temperature 600.00° K				
Translational	41.623207	36.655282	4.967925	4.967925
Rotational	20.090662	17.110147	2.980515	2.980755
Vibrational	5.914995	2.271652	3.643344	7.06974
Total	67.628863	56.037080	11.591784	15.017954
Temperature 700.00° K				
Translational	42.389016	37.421091	4.967925	4.967925
Rotational	20.550147	17.569597	2.980550	2.980755
Vibrational	7.049164	2.874166	4.174998	7.644926
Total	69.988327	57.864854	12.123472	15.593606
Temperature 800.00° K				
Translational	43.052390	38.084465	4.967925	4.967925
Rotational	20.948172	17.967597	2.980575	2.980755
Vibrational	8.103084	3.462689	4.640395	8.139676
Total	72.103645	59.514750	12.588895	16.088356
Temperature 900.00° K				
Translational	43.637527	38.669602	4.967925	4.967925
Rotational	21.299254	18.318659	2.980595	2.980755
Vibrational	9.087226	4.033566	5.053660	8.570010
Total	74.024007	61.021827	13.002180	16.518690

Table II (Continued)

	S	$-(F-H_0)/T$	$(H-H_0)/T$	Cp
Temperature 1000.00° K				
Translational	44.160951	39.193026	4.967925	4.967925
Rotational	21.613308	18.632697	2.980611	2.980755
Vibrational	10.010028	4.585553	5.424475	8.944992
Total	75.784286	62.411275	13.373011	16.893672

* These calculations were made using solid phase frequencies and assuming all vibration to be harmonic. The moments of inertia used to make these calculations are:

I_A = o.341000, I_B = 85.899000, I_C = 86.454000 (AMU) $\mathring{A}^2$

APPENDIX I

LOW FREQUENCY VIBRATIONS OF MOLECULAR CRYSTALS.

Raman and Far-infrared Spectra of HNCS and DNCS

Abstract: The infrared and Raman spectra of polycrystalline HNCS and DNCS have been recorded from 33 to 4000 cm^{-1}. The data have been treated in detail and a vibrational assignment of the six internal fundamentals is suggested. The vibrational data implies a very short N-H---N distance of 2.9 Å. The subsequent structural implications of such a strong H-bond are considered. Evidence was found that HNCS has two distinct crystalline phases and spectra have been recorded for each form. Factor group splitting of the N-H bending fundamental suggests that the crystal has at least four or possibly eight molecules per unit cell depending upon whether or not the crystal is centrosymmetric. Suggested assignments are given for some of the lattice modes.

INTRODUCTION

In an earlier publication[1] we reported the mid infrared spectra of gaseous and solid HNCS and DNCS. The assignment of the out-of-plane skeletal bending mode, ν_6, was stated to be quite uncertain since the only apparent choice gave an extremely high frequency when compared to the similar motions of the HN_3 and HNCO molecules. At the time of our initial investigation, it was not possible for us to obtain the Raman spectrum of this slightly colored material. It was expected that this N=C=S out-of-plane mode might have a reasonable polarizability change and thus be detected in the Raman effect. Therefore, we have investigated the Raman spectra of solid HNCS and DNCS.

Also, in the earlier investigation three definite bands were observed in the spectra of the solids in the vicinity of ν_5, the N-H bending mode. No satisfactory explanation could be given for their origin, although a tentative suggestion of lattice modes was given. We have now investigated the lattice region of the spectrum and evidence has been found for more than one crystalline form. These studies represent a continuation of earlier investigations[2-5] of the frequencies of the lattice vibrations of molecular crystals.

EXPERIMENTAL

The sample of isothiocyanic acid was prepared by the solid-phase reaction of KSCN and $KHSO_4$ at 200°C. The reaction mixture was connected to a vacuum line and the volatile products were trapped in a U-tube immersed in liquid nitrogen. The HNCS which was liberated in the above reaction was purified by pumping on the collection tube at -80°C for a period of 1 hour. To insure that all traces of CS_2, HCN and SO_2 were removed, the sample was pumped on at 0°C for an additional 10 minutes. The purified HNCS was maintained at a temperature of -80°C prior to use so as to prevent decomposition and polymerization. The deuterated isothiocyanic acid was prepared in a similar fashion by reacting KSCN and $KDSO_4$. The isotopic purity of DNCS was confirmed by its mid infrared spectrum.

The Raman spectra of polycrystalline HNCS and DNCS were recorded on a Cary Model-81 Raman spectrophotometer equipped with a Spectra Physics Model 125 He-Ne laser. A cold cell similar to that described by Carlson[6] was used to study the samples at liquid nitrogen temperature. The sensitivity and scanning times were varied to give the optimum resolution and presentation and representative spectra may be seen in Figures 1-3. The instrument was calibrated with the emission lines from a neon lamp and the frequencies for all sharp lines are expected to be accurate to ± 2 cm^{-1}.

The mid-infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. The instrument housing was purged with dry air to remove atmospheric water vapor. The spectrophotometer was calibrated by using standard gases in the higher-frequency region[7] whereas the lower-frequency region[8] was calibrated with atmospheric water vapor. The spectra of the polycrystalline samples were obtained by slowly subliming the compounds onto a silicon support maintained at liquid nitrogen temperature. The far infrared spectra were recorded on a Beckman IR-11 spectrophotometer from 33 to 500 cm^{-1}. The instrument was calibrated with atmospheric water vapor and the assignments of Randall et al[8]. A cold cell, which has previously been described[2], was utilized to study the spectra of the solid samples and typical spectra may be seen in Figure 4. The observed frequencies are summarized in Tables I and II.

RESULTS AND DISCUSSION

Microwave investigations have suggested[9] that HNCS has a relatively short N-H bond distance. Such a result appears to be consistent with the high N-H stretching frequency (3538 cm^{-1}) observed for gaseous HNCS and the large frequency shift which was found upon solidification (538 cm^{-1}). By employing an empirical expression[10] which relates the vapor-solid frequency shift to the length of the N-H--N bond, one calculates a very short N-H--N distance of 2.95 Å for solid HNCS. Such a value implies a very strong hydrogen bond and a similar result has been found for HNCO by X-ray studies[11].

In HNCO the N-H--N separation is 3.07 Å and the molecules are linked into infinite zigzag chains by the hydrogen bonds[11]. Although a similar structure is expected for HNCS, there has been no published data on the crystalline sample. As a result the present vibrational study was undertaken to try and determine whether or not the crystal structure has a center of symmetry. In principal, vibrational spectroscopy can also provide information with regard to the number of phase transitions by studying the spectra at various temperatures; furthermore, the observation of factor group splitting often permits the elimination of certain space groups from consideration.

The emphasis in this study has, of course, been placed on the Raman study since the Raman spectra of this sample has yet to be reported. Thus, we shall discuss the Raman spectra of polycrystalline HNCS and DNCS in some detail prior to considering the low frequency infrared data. It should be pointed out that considerable difficulty was experienced in obtaining the respective spectra, and this is thought to result in part from sampling problems. Thus, despite the fact that the spectra always had a similar appearance, the reproducibility in band centers and relative intensity presented a formidable problem.

Since HNCS is a planar molecule it has C_s symmetry and the 6 fundamental vibrations are permitted in both the infrared and Raman spectra. The normal vibrations belong to the following irreducible representations: 5 a' + 1 a". The vibrations of a' symmetry may be described approximately as: an N-H stretch (ν_1), a C=N stretch (ν_2), a C=S stretch (ν_3), an in-plane C=N=S bend (ν_4), and an N-H bend (ν_5). The only vibration of a" symmetry is the C=N=S out-of-plane bend (ν_6). It should be noted that since ν_6 is the only vibration of a" symmetry, the Teller- Redlich product rule predicts that it should not shift upon N-deuteration.

RAMAN SPECTRA

The Raman spectra of HNCS have been reproduced in Figs. 1 and 2 whereas the spectrum of DNCS may be seen in Fig. 3. In Fig. 1 the spectrum is quite simple and there is no apparent doubling of the two skeletal stretching modes as was observed in the spectrum reproduced in Fig. 2. It should be noted that each of the spectra of HNCS were obtained approximately an equal number of times and that it was not actually possible to predict when either spectrum would be observed. This was a very disturbing factor, but it is most likely a result of the sampling difficulties encountered. For example, the design of the low temperature Raman cell is such that partial annealing of the sample always occurs when the brass rod which contains the sample is placed against the light pipe which is initially near room temperature. With this design, different degrees of annealing always seem to result and this is probably quite dependent on the amount of sample on the brass rod. Because the low frequency spectral region in both Figs. 1 and 2 are so well defined, it is thought that each spectrum results from a different crystalline form rather than a "glass" phase. The spectra of DNCS always appeared to correspond to the HNCS spectrum shown in Fig. 2 with each made showing the expected shift factor. No spectrum of DNCS corresponding to that observed in Fig. 1 for HNCS was ever obtained.

There is little question about the assignment of the N-H stretching fundamental since it has a well-established group frequency. Thus the band at $\sim$3000 cm^{-1} in HNCS shifts upon N-deuteration to 2326 which confirms the assignment to an N-H motion. As previously noted the large vapor-solid frequency shifts result from the formation of relatively strong hydrogen bonds.

The two skeletal stretching modes in HNCS may be approximately described as C=N and C=S motions, respectively. These motions should involve a large polarizability change and, thus, should give rise to relatively intense Raman lines. For KNCS the C=N and C=S stretching modes were observed[12] at 2053 and 749 cm^{-1}, and similar frequencies were expected for polycrystalline HNCS. Therefore, the lines at 1934 and 851 cm^{-1} in Fig. 1 have been attributed to the fundamentals in HNCS which involve primarily C=N and C=S motions, respectively. In addition to the bands at 1934 and 851 cm^{-1} shown in Fig. 2, lines were also observed at 2055 and 789 cm^{-1}. Several possible explanations can be given for the origin of these bands. Foremost is the possibility that the spectrum shown in Fig. 2 represents that of a second phase of solid HNCS and the doubling of the two skeletal modes can be attributed to factor group splitting. Also it should be pointed out that the spectrum shown in Fig. 2 may actually be a composite of the spectra from two crystalline modifications. However, since the relative intensities of both doublets remain always the same, this alternative does not appear to be as attractive as the former one. A third possible explanation is that the different spectra are due to orientational phenomena; however, because of the polycrystalline nature of the sample, such an interpretation does not seem very probable.

The spectrum of DNCS in the region of the two skeletal stretching modes is somewhat more complicated than that for the "light" molecule. The two rather strong lines at 1874 and 1931 cm^{-1} both have high frequency shoulders (see Table 1). Additional splittings have been previously reported for other deuterium compounds so the increased complexity is not totally unexpected[13]. The two lines assigned to ν_3 are very similar for both molecules but the lines in both spectra are considerably broader than those assigned to ν_2 and the additional splitting would be much more difficult to detect for ν_3.

In conclusion, on the basis of the current evidence, it seems certain that two crystalline modifications of HNCS exist and the observed spectra correspond to the two different phases.

The fact that the low frequency region of the Raman spectra is nearly the same in Figs. 1 and 2 is somewhat surprising. However, if the number of molecules per unit cell is doubling then the in-and out-of-phase motions of the intermolecular modes may only cause a broadening or slight splitting of the lattice modes. Only the 103 cm^{-1} line shows a definite splitting in the spectrum shown in Fig. 2.

Unfortunately neither of the skeletal bending nor the N-H bending modes were observed in the Raman spectrum. For the linear "NCS" moiety, the skeletal bending mode would not be Raman active so apparently the presence of the hydrogen atom does not provide sufficient "perturbation" to give Raman activity to the skeletal bending modes. The N-H bending modes are frequently quite weak in the Raman effect[14,15].

A summary of the frequencies observed for both HNCS and DNCS are listed in Table I. The low frequency lines at 72 and 44 cm^{-1} for the "light" molecule were observed at 70 and 44 cm^{-1}, respectively, in the spectrum of DNCS. As such these lines are attributed to motions of translatory origin. The line centered at 95 cm^{-1} for HNCS appears to shift to 85 cm^{-1} upon deuteration which suggests that it results from a librational mode. The band located near 200 cm^{-1} shows little change with deuteration and is believed to represent a stretching mode of the N-H---N hydrogen bond. This frequency is in the range observed for the O-H---O bond and reflects the strength of the hydrogen bonding in HNCS. The ramifications of the Raman spectra on the crystal structure will be considered in a later section.

Mid-Infrared

In Fig. 4 is shown the mid infrared spectrum of HNCS with repeated annealing to both -150^{0}C and -115^{0}C. The spectra were taken with a silicon substrate since the alkali halides initiate decomposition[16]. The spectrum indicated as B probably represents a glass since the sample was sprayed on the substrate, which was maintained at liquid nitrogen temperature, and it was not annealed. The spectrum represented in Fig. 4 C is that of a sample which was repeatedly annealed to -150^{0}C until no further changes were noted in the spectrum. One readily notes that the N-H stretching mode shifts to lower frequency, and the skeletal stretching mode at 2008 practically disappears. Also, relatively strong bands are observed at 900 and 502 cm^{-1} and a very complex absorption is centered near 475 cm^{-1}.

The spectrum reproduced in Fig. 4 D was obtained after the sample was repeatedly annealed to -115^0 C. The spectral changes are again quite dramatic since the shoulder at 2060 cm^{-1} in Fig. 4 C is now an intense band. Additionally, a new band is seen at 682 cm^{-1} and the absorption centered near 457 cm^{-1} consists of four sharp bands. The bands at 457 cm^{-1} are believed to result from ν_5, the N-H bending fundamental. The fact that four bands are observed implies that there are at least four molecules per unit cell. Upon warming the sample to its melting point, and then rapidly cooling it, the spectrum in Fig. 4 E results. The strong bands at 1950 and 903 cm^{-1} have disappeared and the remaining bands have been assigned to the six fundamental modes as may be seen in Table IV. The most reasonable explanation of the disappearance of the bands at 1950 and 903 cm^{-1} is that more than one crystalline phase was giving rise to the spectra in Figures 4 C and D, whereas only a single phase results after the sample has been annealed to its melting point (Fig. 4 E). The frequencies observed for the C=N stretching mode (ν_2) in the infrared and Raman spectra do not coincide. Such a result suggests that the molecules are arranged in a centrosymmetric fashion and thus, there may actually be at least eight, rather than four molecules per unit cell.

It should be pointed out that the band at 619 cm^{-1} in each trace shown in Fig. 4 results from the silicon plate. The out-of-plane skeletal bending mode, which has not previously been observed, has been assigned to the band at 682 cm^{-1}. Such an assignment appears reasonable since ν_6 was originally[1] thought to be somewhere between 600 and 800 cm^{-1}. Despite the fact that the frequency difference between the a' and a'' skeleton bending modes is relatively large, the 682 cm^{-1} band appeared in both Figs. 4 D and E and it may well be concealed by the breadth of the 770 cm^{-1} band in Fig. 4 C. No reasonable combination or overtone assignment could be established for this band; furthermore, factor group splitting does not appear realistic on the basis of the observed splitting of the N-H bending fundamental. On the basis of the current experimental evidence, then, ν_6 has been tentatively assigned to the 682 cm^{-1} band.

Far-Infrared

The far-infrared spectra of HNCS and DNCS may be seen in Figs. 5 and 6, respectively. Each spectrum was obtained from a freshly deposited sample which had been annealed to different temperatures. Although the spectra appear to have some differences, on the whole there is essentially a one-to-one correspondence in the number of bands observed (see Table IV). The spectra in Figs. 5 B and C are thought to correspond, respectively, with those of the mid-infrared shown in Fig. 4 C and D. In Fig. 5 D, three bands appear in the region of 150 to 225 cm^{-1}, whereas only a single band was resolved in the upper traces, although there is some indication of a shoulder near 160 cm^{-1}. The lower frequency bands in all three spectra appear to correspond, but there is an obvious intensity variation. The bands centered at 195, 109, and 92 cm^{-1} (Fig. 5 B) have been attributed to lattice modes, whereas the bands in the

500 cm^{-1} region have previously been ascribed to ν_4 and ν_5. The weak feature in the low frequency spectrum of HNCS centered near 300 cm^{-1} probably results from a multiphonon process.

In the spectrum of DNCS (see Fig. 6 B), the bands at 200, 108, and 88 cm^{-1} are believed to correspond to the bands of similar frequency in HNCS (Table IV). The weak bands at 329, 278, and 255 cm^{-1} may be a result of multiphonon transitions. The spectrum shown in Fig. 6 C is thought to correspond with that of 5 D where one has again observed a greater multiplicity of bands in the 150-200 cm^{-1} region. Clearly, the far-infrared spectra of HNCS and DNCS are very similar. The fact that we obtained what appear to be two different spectra suggests that the spectral changes result from distinct phases. The far infrared bands of both isotopic species were quite distinct and in no instance did annealing result in broad bands characteristic of the lattice spectrum of a polymer or decomposed material. Although there has been no detailed report of the number and structure of the phases in HNCS, the oxygen analog (HNCO) is known to have two stable crystalline phases.[11] Thus it is concluded that when the isothiocyanic acid crystal is annealed to -150°C a phase which we will designate as Phase II is obtained, and is mainly represented by the spectra in Figs. 4 C and 5 B. When the sample is further annealed to -115°C a second crystalline phase is obtained which can be designated as Phase I. The spectra in Figs. 4 D, 5 C and 6 B are all believed to be representative of this phase. The spectra shown in Figs. 5 D and 6 C are also believed to originate from samples in Phase I, but with different relative orientations of the H-bond in reference to the incident radiation. There can be little doubt that the relatively strong band near 200 cm^{-1} originates from the N-H---N stretching motion and it may be possible to grow crystals with different relative orientations of this bond in relation to the substrate. These two types of spectra appeared randomly and neither spectra could be obtained preferentially by changing the sampling techniques. As evidenced in Tables I and IV, the low frequency infrared and Raman bands do not correspond exactly in frequency. Because of this fact and the previously mentioned sampling problems, it is actually not possible to uniquely assign this spectral region, although there is little doubt these bands result from external modes.

Summary and Conclusions

The infrared and Raman spectra of polycrystalline HNCS have been recorded and a vibrational assignment is suggested for the six internal fundamentals. The previously unassigned out-of-plane skeleton bending mode has been tentatively assigned to the band at 682 cm^{-1}. The infrared and Raman counterparts of the C=N stretching fundamental were widely separated which suggests that the crystal structure may be centrosymmetric. Factor group splitting was observed for several of the bands and was most apparent for the N-H bending vibration where four bands were clearly defined. On the basis of the observed factor group splitting for ν_5, it would appear that HNCS has at least four or eight molecules per unit cell depending upon whether or not it has an inversion center. The vibrational data also provides strong evidence for the existence of at least two different crystalline phases, and the vapor-solid frequency shift for ν_1 suggests a relatively short N-H---N distance.

Acknowledge

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Table I. Raman Spectra of Solid HNCS and DNCS.

HNCS		DNCS	Assignment
Phase I	Phase II	Phase II	
44 vs	44 vs	44 vs	lattice
72 vs	72 vs	70 vs	lattice
	95 s	85 s	lattice
103 s	104 s	98 sh,w	lattice
		117 sh, m	lattice
196 s	196 s	201 s	lattice
	312 w		second order line
	789 m	789 s	ν_3 C=S stretch
851 s	851 s	843 s	
		930 w	
		1059 w	
		1295 w	
		1440 m	
		1874 s	
1934 m	1934 m	1890 m	ν_2, C=N stretch
	2055 m	1931 s	
		1946 m	
		2326 m	ν_1, N-D stretch

Table II. Mid Infrared Spectra of Solid HNCS (-190°C)

B	C	D	E
		3385 W	3380 VW
3170 S-B	3030 S-B	3020 S-B	3000 S-B
	2100 W		
2008 S	2080 W	2098 W	2100 W
1930 S	2060 W	2062 S	2060 S
	1950 S	1950 S	2010 M
1505 M	1503 W	1510 VW	-
860 W	900 S	903 S	825 W
			788 M
755 M	770 S	775 S	768 M
		682 M	682 M
			650 VW
555 W-B	502 S	500 S	498 S
	468 W	467 W	468 W
465 W	457 M	455 M	456 M
	427 W	440 M	441 M
420 W	410 VW	421 M	423 M

1) not annealed

2) annealed to -150°C

3) annealed to -115°C

4) annealed to -103°C (M.P.)

Table III. Far Infrared Spectra of Solid HNCS and DNCS (-190°C)

HNCS	HNCS	HNCS	DNCS	DNCS
B	C	D	B	C
	92 W	86 M	88 W	86 M
106 M	109 S	109 M	108 W	113 W
		155 S		149 S
195 VS	195 VS	195 S	200 VS	188 S
		225 M	255 W	
315 W	310 W	300 W	278 W	290 M
	432 W		329 W	
	447 M		415 M	410 M
472 M	458 M		463 S	440 S
	471 M			458 S
				540 S
515 S	515 S			

Table IV

Summary of the Fundamental Vibrations of HNCS

Fundamental and Symmetry Species	Infrared Solid (cm^{-1})	Assignment
a'		
1	3000	N-H Stretch
2	2068, 2010	Skeleton Stretch (C=N)
3	788, 768	Skeleton Stretch (C=S)
4	498	Skeleton Bend
5	468, 456, 441, 423	N-H Bend
a"		
6	682	Skeleton Bend

FIGURE CAPTIONS

Figure 1 Raman spectra of solid HNCS (-190°C) phase I.

(A) Single slits.

(B) Double slits.

Figure 2 Raman spectra of solid HNCS (-190°C) phase II.

(A) Single slits.

(B) Double slits.

Figure 3 Raman spectra of solid DNCS (-190°C) phase II.

(A) Single slits.

(B) Double slits.

Figure 4 Mid-infrared spectra of polycrystalline HNCS (-190°C) recorded on a silicon substrate.

(A) "Background" spectrum of the cell.

(B) Spectrum of rapidly deposited HNCS; the sample was not annealed.

(C) Spectrum of HNCS annealed to -150°C.

(D) Spectrum of HNCS annealed to -115°C.

(E) Spectrum of HNCS annealed to -103°C (melting point).

Figure 5 Far infrared spectra of solid HNCS (-190°C).

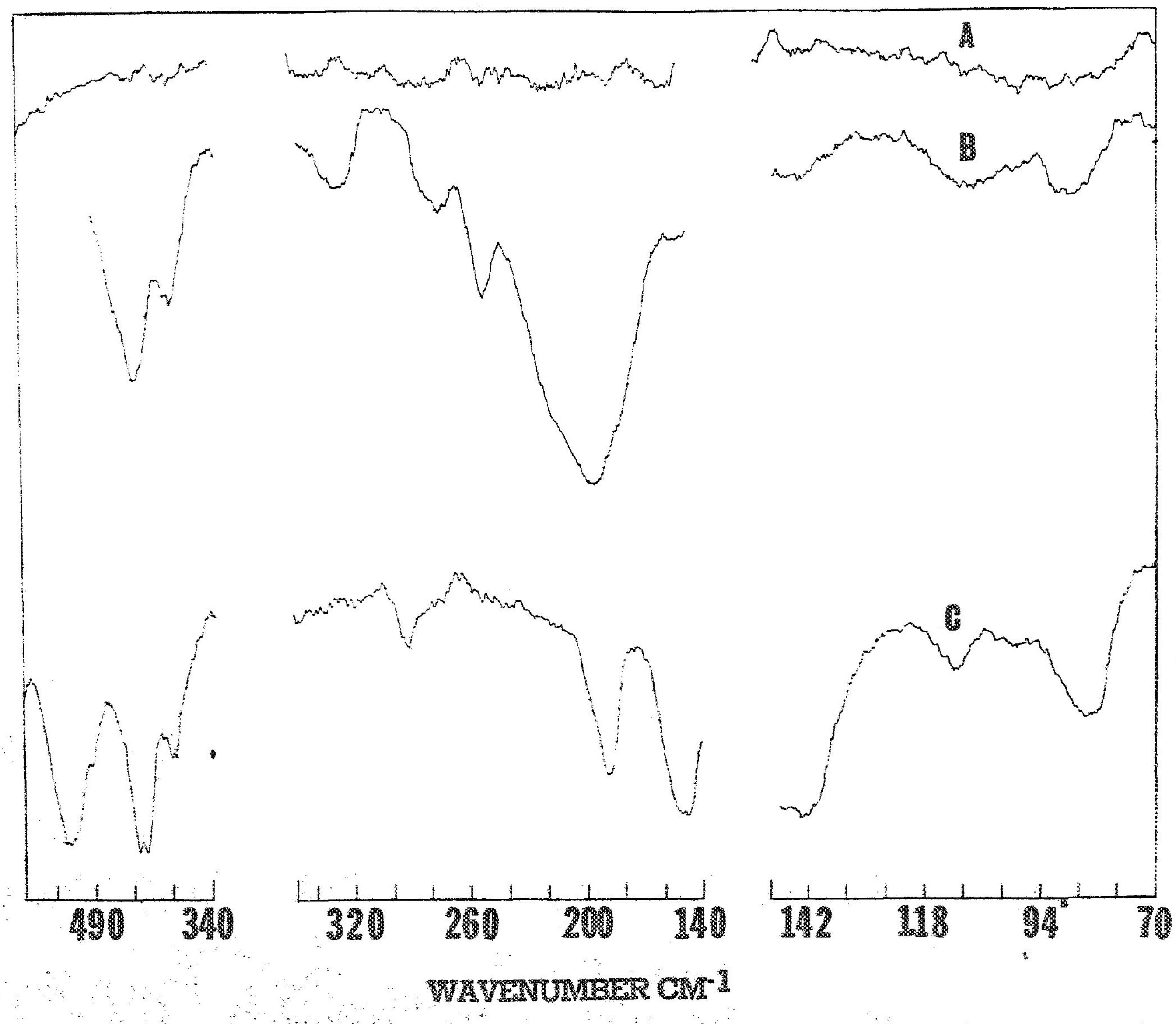
(A) "Background" spectrum of the cell.

(B), (C), and (D) Represent different depositions of HNCS which have been annealed to different temperatures.

Figure 6 Far Infrared spectra of solid DNCS (-190°C).

(A) "Background" spectrum of the cell.

(B) and (C) Represent different depositions of DNCS which have been annealed to different temperatures.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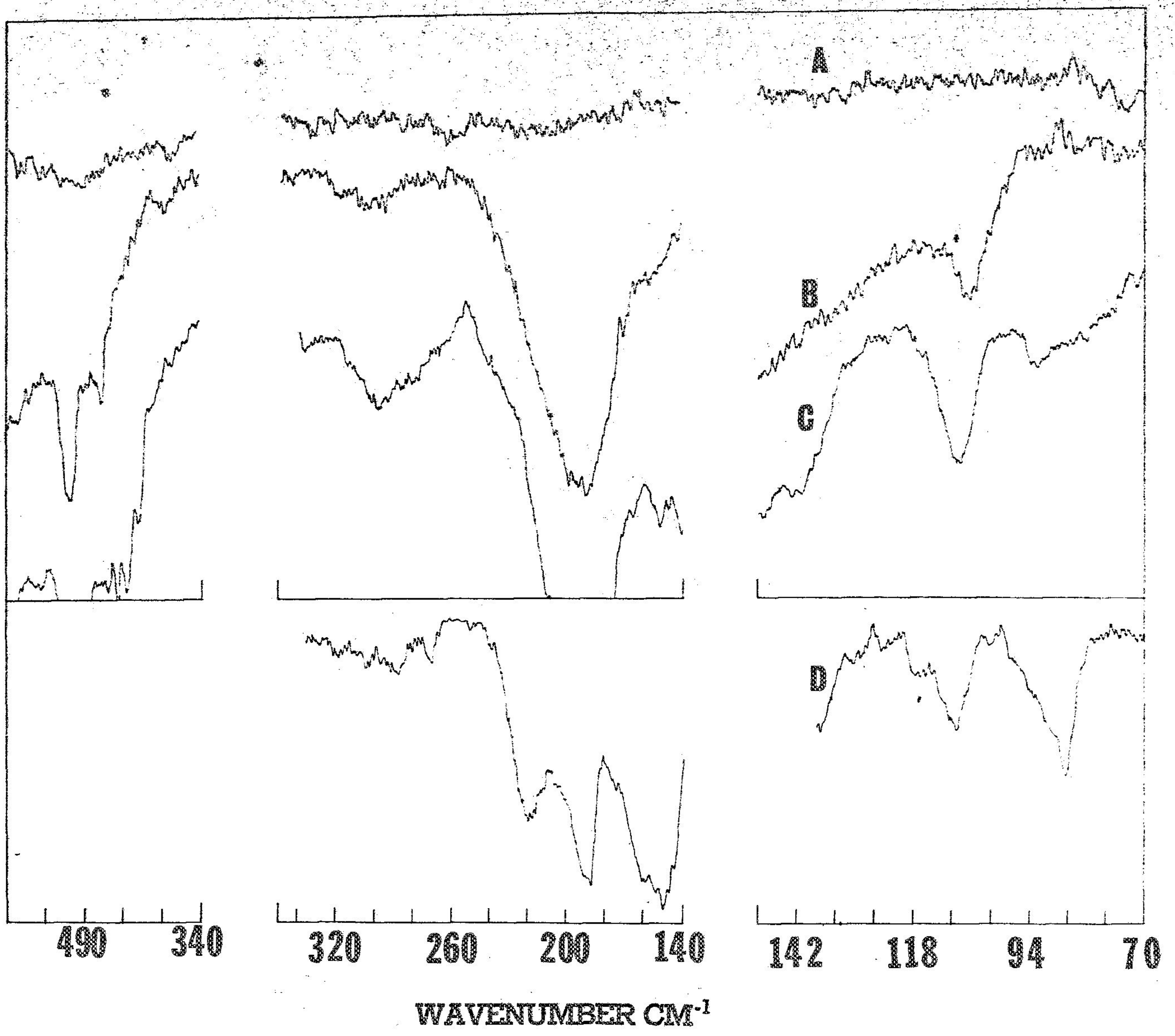
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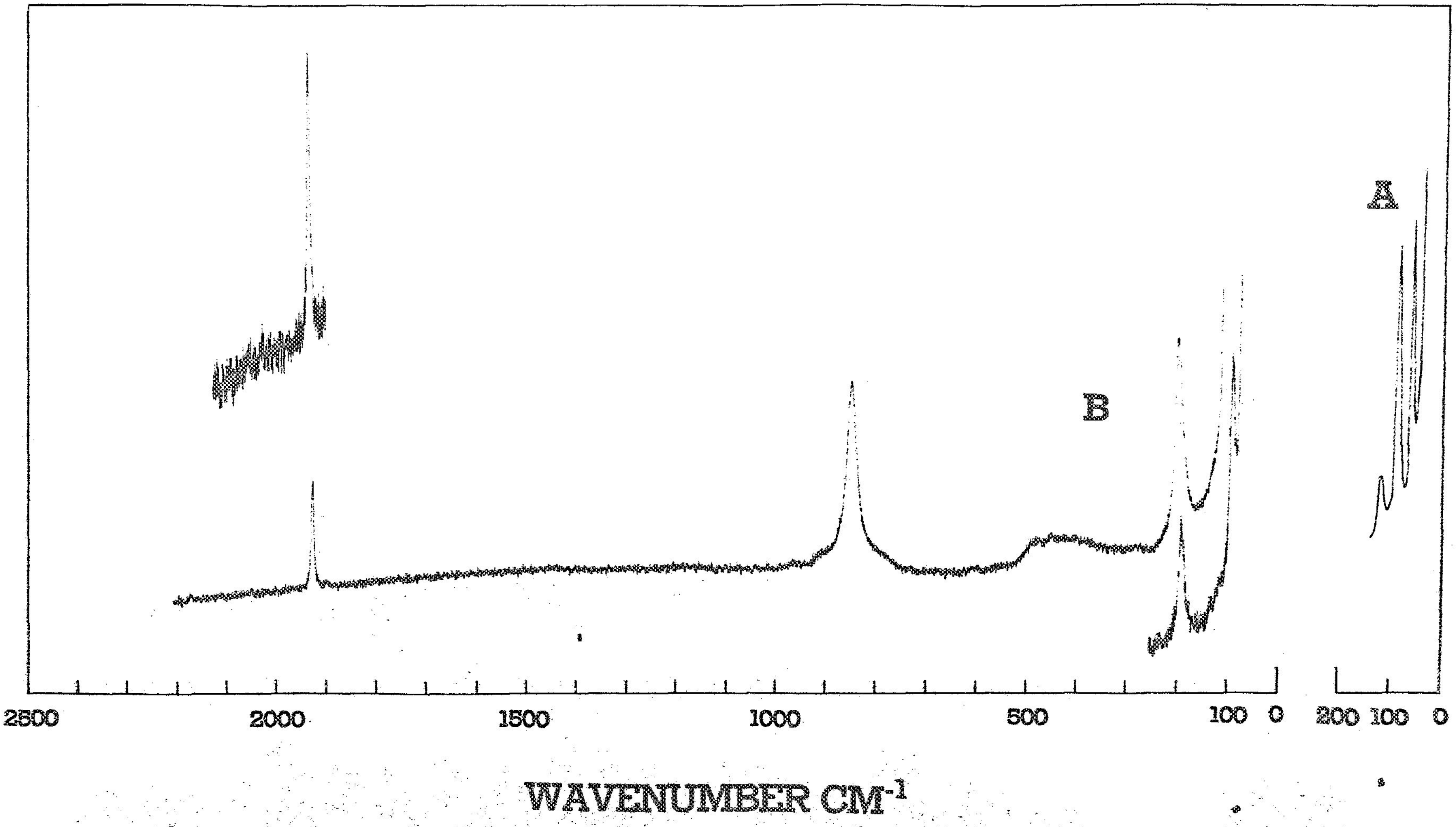
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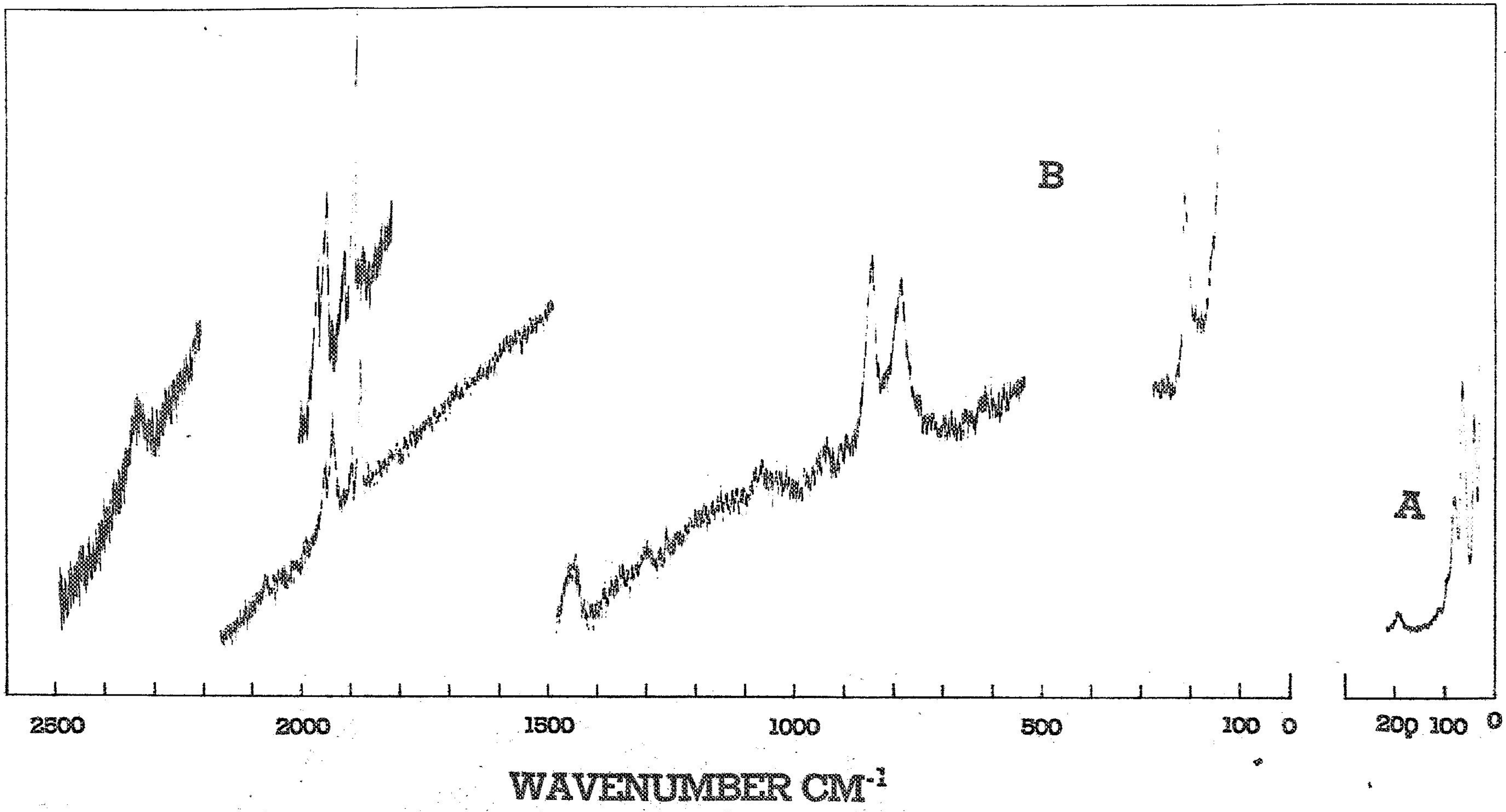
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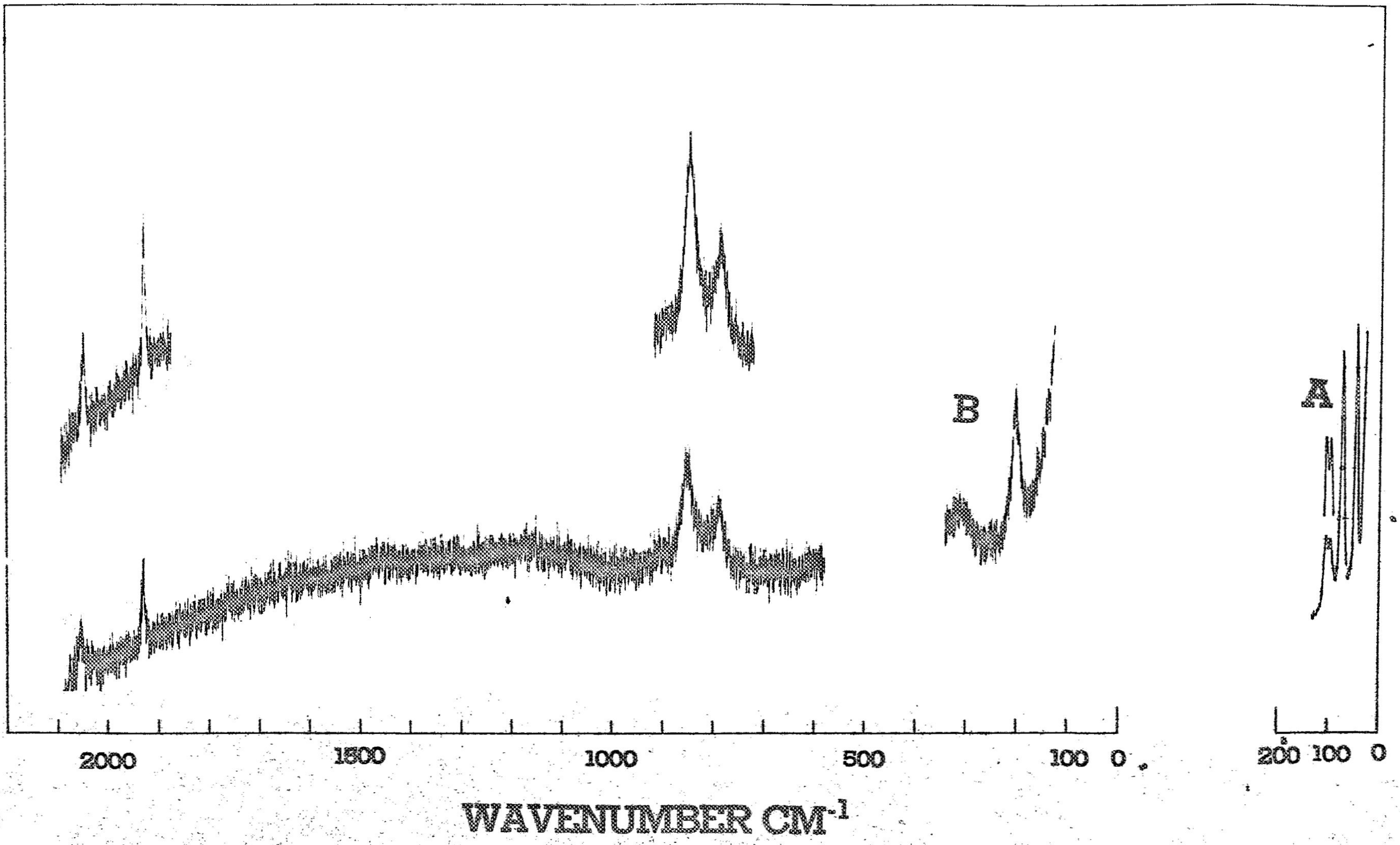
WAVENUMBER CM^{-1}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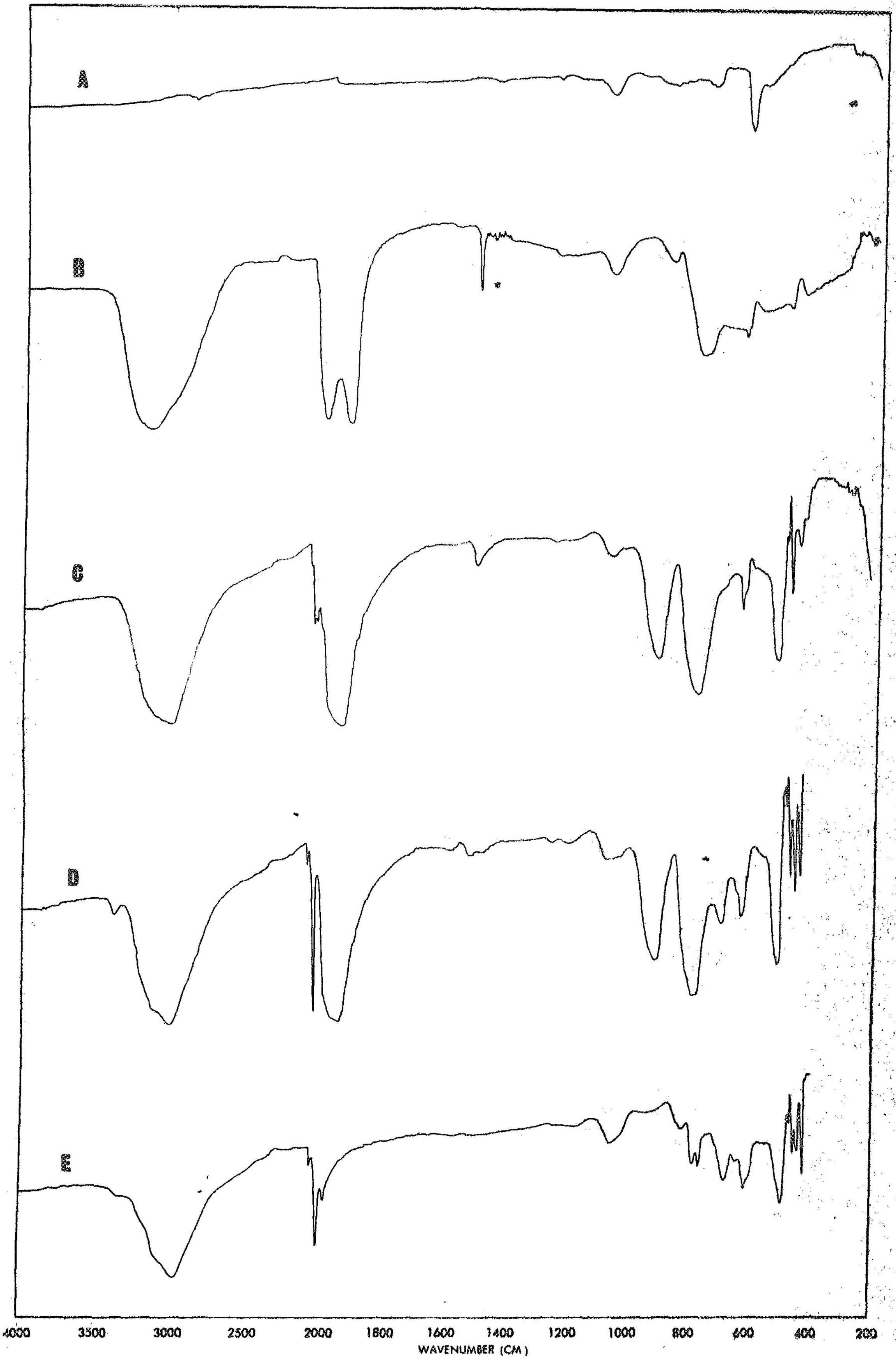
WAVENUMBER CM^{-1}


A
B
C
D
E
*
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3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM)

APPENDIX II

Vibrational Spectra and Structure of Oxalyl Fluoride in the Solid and Fluid States

Abstract: The vibrational spectra of oxalyl fluoride have been examined in the solid phase and re-examined in the fluid phases. From the disappearance of three major bands upon solidification, it is concluded that there must be two isomeric forms in the vapor. The spectra have been assigned on the basis of two isomers; solid-phase frequencies were used for the trans fundamentals and bands unique to the fluid states were assigned to the cis isomer. The values observed for the fundamentals in the solid are compared to those previously reported from studies of the fluid states. The internal torsion was observed at 54 cm^{-1} in the vapor state, and a barrier to internal rotation of 12.4 kcal/mole has been calculated. A comparison of the infrared and Raman bands in the crystal shows that the mutual exclusion principle is operative. It is concluded from this alternate forbiddance that the molecule has a centrosymmetric structure in the crystal and that each molecule occupies a C_i site. The factor group of the crystal is believed to be either C_{2h} or D_{2h} with two or four molecules per primitive cell.

INTRODUCTION

Molecules in the series of halogenated oxalic acids have been the subject of considerable controversy, with respect to the possibility of cis or trans structure, or both.[1-8] Recent work at this laboratory has shown oxalyl chloride[9] and bromide[10] to exist in both isomeric forms in liquid and vapor phases. However, spectra of crystalline samples of these compounds showed complete conversion to the trans form upon solidification. The last reported vibrational study of oxalyl fluoride[6] concluded the molecule exists in only the trans form, and the spectra were interpreted on this basis. Since this compound has not been studied in the crystalline phase, work has been undertaken to determine if the fluoride behaves in a manner comparable to the other oxalyl halides and to observe possible crystalline effects.

The infrared spectra have been obtained for the solid and vapor phases and the Raman spectra for the solid and liquid phases. The results will be presented and shown to be consistent with the presence of two isomers in the fluid states. Also of particular interest was the frequency for the internal torsional oscillation.

EXPERIMENTAL TECHNIQUES

Oxalyl fluoride was prepared by the method given by Hencher and King.[6] A solvent system of 50g sulfolane and 26g NaF was stirred, with slight heating, for ∿24 hr, under reduced pressure. After venting, a dropping funnel containing ∿10 ml $(COCl)_2$ was added to the system. The reaction was then run in a closed system, collecting product in a liquid nitrogen trap. Oxalyl chloride was added dropwise with a reflux column maintained at -5°C for a time of ∿3 hr. Slight heating was begun after all the chloride had been added. It was found that nearly pure $(COF)_2$ could be obtained if the temperature was raised very slowly and a good reflux was maintained.

Infrared spectra for the vapor and solid phases were recorded on a Perkin-Elmer Model 621 spectrophotometer between 4000 and 200 cm^{-1} and on a Beckman IR-11 between 500 and 33 cm^{-1}. Both instruments were purged with dry air and calibrated with standard gases. Vapor-phase samples were contained in a 20-cm cell equipped with cesium bromide windows in the mid-infrared region and in a Beckman 10-m variable-path gas cell equipped with polyethylene windows in the far-infrared region. Spectra of the solid were obtained from thin films deposited in vacuum onto a cesium iodide or silicon plate cooled by boiling nitrogen.

Raman spectra were recorded with a Cary 81 spectrophotometer equipped with a helium-neon laser for excitation. The instrument was calibrated with emission lines from a neon lamp over the spectral range 0-4000 cm^{-1}. The liquid sample was sealed in a glass capillary tube. The solid sample was prepared by spraying the material on the end of a brass rod, cooled with liquid nitrogen and then placing this sample against a light pipe.

RESULTS

The infrared spectra of $(COF)_2$ vapor and solid are presented in Fig. 1, the Raman spectra of the liquid in Fig. 2, and of the solid in Fig. 3. There are notable differences between the infrared spectra of vapor and solid samples, and at least three important bands essentially disappear upon solidification (1897, 1267, and 799 cm^{-1}; See Fig. 4.). The Raman spectra do not show the same contrast. Oxalyl fluoride is a very poor Raman scatterer, and it was necessary to record the spectra with a poor signal to noise level. Comparison of our results with those previously published by Hencher and King[6] suggests that the sample used in their Raman study contained an impurity, but it does not appear to be oxalyl chloride fluoride, a likely suspect. Several bands they report as having moderate relative intensities are not observed in our spectra at all. For example, the Raman lines at 292 (6), 565 (3), and 627 (0) (a relative intensity of 16 is listed for the 420 cm^{-1} line) were not observed in our spectrum. The 292 cm^{-1} line was almost one-half as intense as the 420 cm^{-1} line and it was assigned as the COF rocking fundamental. The only pronounced disappearance of a band from the Raman spectrum is found at the 420 cm^{-1} line. This line is definitely made up of two components with frequencies of 415 and 420 cm^{-1} with the higher frequency line being less intense. However, only one Raman line was found in the spectrum of the solid in this frequency range. The bands observed in solid oxalyl fluoride are summarized in Table I.

It is apparent from Fig. 1 that the infrared bands at 1897, 1267 and 799 cm^{-1} disappear upon solidification. This can be made to occur as a step-wise process. If the sample is condensed quickly, these bands appear in the solid. However, as the sample is annealed to the stable crystalline state these bands disappear. Figure 4 shows two steps in the annealing process. Taking as fundamentals of the <u>trans</u> isomer those bands which remain in the samples of good crystallinity, it is not possible to fit those bands that disappear as differences tones. It should also be noted that the intensity of difference tones is a function of <u>temperature</u> only and not a function of crystallinity! There is one possible conclusion. These bands must be due to a less stable form of oxalyl fluoride and it is assumed to be the <u>cis</u> isomer. The lack of a similar disappearance of bands from the Raman spectrum may indicate that the <u>cis</u> form exists in low ratio in the liquid or it may merely be a consequence of the weakness of th entire spectrum. This is not felt to be evidence against two isomers, since the difficulty encountered in obtaining a good Raman spectrum of the <u>trans</u> fundamentals justifies little hope of observing many of the <u>cis</u> modes by this technique. Since some Raman bands of <u>cis</u> oxalyl bromide and chloride were observed, it seems likely that the problem with the fluoride is mainly one of intensity. The <u>trans</u> form should be the most stable configuration, considering steric and electrostatic effects[11]. If one assumes that the carbonyl double bond can be represented by two "bent" single bonds,[12] then the <u>trans</u> configuration is equivalent to the staggered form of ethane which is, of course, the more stable form. Thus the <u>cis</u> structure represents the eclipsed form and it is not expected to be nearly as stable.

A consideration of the frequencies in the infrared and Raman spectra of the solid state shows that the rule of mutual exclusion is operative and the molecule exists entirely in the trans configuration in this phase. The crystal structure has not been determined, but in the cases of both the chloride and bromide a center of inversion is maintained in the crystal, so that mutual exclusion remains. It appears that the fluoride molecules also occupy C_i sites in the crystal since a one to one correspondence between the internal modes of the crystal and those predicted for the isolated molecule (C_{2h}) is observed.

Variable-temperature studies were attempted in the infrared, both by raising and lowering the temperature of a gaseous sample from room temperature. Unfortunately, neither method gave reliable information on the value of the ΔH for the cis-trans conversion. Oxalyl fluoride decomposed on raising the temperature, and there was no consistency in the cis (1267) and trans (1097) peak ratios as the temperature was raised. Cooling of the gas from room temperature to -61°C produced only slight changes in the two peaks. Therefore, we were not able to calculate the thermodynamic quantities for isomerization.

VIBRATIONAL ASSIGNMENT - trans $(COF)_2$

From group theory one predicts six fundamentals ($5 a_g + b_g$) in the Raman effect and six normal modes ($2a_u + 4b_u$) in the infrared spectrum of trans-oxalyl fluoride. The six infrared bands are fairly readily discernable from the solid-phase spectrum. In the mid-infrared region, the strong bands at 1857, 1122, 676, 461 cm^{-1}, and the weaker band at 265 cm^{-1} are obviously fundamentals. The torsional vibration has been found in the far-infrared spectrum of the solid at 94 cm^{-1} (Fig. 5) and at 54 cm^{-1} in the spectrum of the vapor (Fig. 6). There are no other strong bands to choose from in the spectrum of the solid. These infrared-active fundamentals have been assigned as follows: 1857 to ν_9, the antisymmetric C=O stretch; 1122 to ν_{10}, the antisymmetric C-F stretch; 676 to ν_{11}, the antisymmetric FCO bend; 461 to ν_6, the FCO out-of-plane deformation; 265 to ν_{12}, antisymmetric FCO rock;

and 94 to ν_7, the torsion.

The case is less conclusive for the Raman-active modes. At first glance, there appear to be only three main bands to be assigned as fundamentals. Because of the small polarizability of the fluorine atom[13], modes involving fluorine motion are expected to give rise to weak Raman bands, a phenomenon that is well documented[14]. This led to a more thorough search for the weak fundamentals. The three main Raman bands at 1866, 812, and 420 cm^{-1} are assigned, respectively, to ν_1, ν_3, and ν_5, the symmetric C=O stretch, C-C stretch, and symmetric FCO rock. The symmetric C-F stretch, ν_2, is observed as a weak band at 1290 cm^{-1}. This is at a higher frequency than expected and the C-C stretch occurs lower than in analogous compounds (see Table II). The C-F stretch of the FCO radical[15] has been observed at 1018 cm^{-1}, and the C-C stretch[9,10] in $(COCl)_2$ occurs at 1093 cm^{-1} and in $(COBr)_2$ at 1025 cm^{-1}. The frequency shifts for the C-F and C-C stretching modes are apparently caused by a perturbation resulting from the C-F stretch falling at a frequency very close to that of the normal C-C stretching motion. Both bands are shifted, one to a higher and the other to a lower frequency by approximately the same amount. The average of the observed frequencies gives a value of 1056 cm^{-1}. This is in line with the other oxalyl halide C-C stretching frequencies and also consistent with the value for the C-F stretch of the FCO radical. A similar assignment was given to these modes in the molecule $(CF_3)_2C{=}C{=}O$: the Raman active symmetric C-F stretch occurring at 1199 cm^{-1} with relative intensity 5 and the symmetric C-C stretch at 766 cm^{-1}, intensity 100[16]. On the basis of the relative intensity of the 812 cm^{-1} Raman line there can be little doubt that this band is due to mainly C-C stretching motion. The reverse assignment of these bands would require the ascribing of a large polarizability change to the C-F stretching motion. This is contrary to the experimentally established data for this normal mode.

Two very weak bands at 595 and 513 cm^{-1} have been assigned to ν_4 and ν_8, respectively, the symmetric FCO bending and FCO out-of-plane bending motions. These were the only two Raman bands observed in the frequency region expected on the basis of earlier studies (see Table II). The assignments of all bands (combination and fundamentals) observed in the spectrum of solid oxalyl fluoride are listed in Table I and descriptions of the trans fundamentals are given in Table III.

As stated earlier the torsion, ν_7, was observed in the gas phase at 54 cm^{-1} (Fig. 6). A reduced moment of inertia F value of 0.672 cm^{-1} was calculated by the method of Pitzer[17] using structural parameters assumed by Hencher and King[6]. These parameters led to a barrier to internal rotation of 12.4 kcal/mole, in good agreement with the barriers for glyoxal,[18] diacetyl[19,20] and oxalyl chloride[9], which are, respectively, 13.7, 10.1, and 11.1 kcal/mole. These barriers apparently reflect the relative insensitivity to substituents of the torsion around the carbon-carbon bond for these substituted oxalyl compounds. Such insensitivity to substitution has been found for the barriers to methyl rotation in the acetyl-aldehyde derivatives. The relative values for the V_1, V_2 and V_3 terms in the series expansion of the torsional potential energy function have not been determined for any of the oxalyl compounds. Such a determination requires three pieces of experimental data and only one torsional frequency and the ΔH of isomerization have been obtained for the other two oxalyl halides. For the fluoride, only the torsional frequency was obtained and it is not possible to even give limits for the relative magnitudes of the expansion terms as was done for the bromide.

VIBRATIONAL ASSIGNMENT - Cis $(COF)_2$

A partial assignment for the cis isomer has been made from the bands observed in the fluid phases but missing in the solid. As mentioned earlier, there is only one additional Raman band. For the molecule with C_{2v} symmetry, however, only two of the twelve vibrations, the a_2's are Raman active only. The $5a_1$,$4b_1$,and $1b_2$ modes are both infrared and Raman active. There are several combination bands to aid in their assignments, as well. The three prominent infrared bands at 1897, 1267, and 799 cm^{-1}, present only in the vapor-phase spectrum, have been assigned to the antisymmetric C=O stretch, antisymmetric C-F stretch, and the C-C stretch, respectively. From the combination band at 3766 cm^{-1} (gas only), the symmetric C=O stretch can be calculated to be approximately 1869 cm^{-1} (3766-1897=1869) and would be obscured by the trans band at 1865 cm^{-1}. The ν_{11} gas-phase band of the trans isomer appears to have an "extra" P branch in its PQR structure, and this has been taken for a cis fundamental, along with the Raman band at 415 cm^{-1}. The 664 cm^{-1} band is assigned to an FCO bend and the 415 cm^{-1} Raman line to an FCO rocking motion. These latter two assignments must be considered quite tentative and there appears to be little value in the speculation of the frequencies for the remaining fundamentals of this isomer. However the lack of definite assignments for the other normal modes of the cis isomer does not invalidate the conclusion that there are two isomers in the fluid states of oxalyl fluoride since one rarely finds different frequencies for all of the fundamental vibrations of a second isomer.[11] In Table IV are summarized the assignments for all of the observed bands in both the fluid and solid states.

DISCUSSION

The vibrational work on the series of compounds, $(COCl)_2$, $(COBr)_2$, and $(COF)_2$, leaves little doubt that there are two isomeric forms in the gas phase. It is interesting that glyoxal[18] and 2,3-butadione[20] exhibit only one form which leads one to the conclusion that the halogens provide a stabilizing influence for the cis configuration. This stabilization can be rationalized on the basis of the relative magnitude of the non-bonded forces between the halogens and the carbonyl group. For example, Saegebarth and Wilson[21] found the stable configurations of fluoroacetyl fluoride to be the trans and the unexpected cis configuration. These data clearly demonstrated the stabilizing influence of the fluorine-fluorine interaction. On this basis one then expects the halogen-substituted oxalyl compounds to be the most favorable for the observation of a cis isomer.

Hencher and King's conclusion that oxalyl fluoride exists only in the trans form[6] in all phases demonstrates the importance of taking spectra of the solid phase for the detection of isomers. They used only gaseous infrared and liquid Raman samples to obtain their vibrational data. The contamination of their Raman sample also contributes to the uncertainty of their vibrational assignment. Our solid-phase work clearly demonstrates the structural difference that exists between the rigid and fluid phases of the oxalyl fluoride molecule.

The apparent factor group splitting of the C-C stretching vibration suggests that there are at least two molecules per unit cell. From the mutual exclusion it was concluded that the oxalyl fluoride molecule is centrosymmetric in the crystal and the molecules probably occupy C_i sites. For molecules occupying such sites, packing considerations suggest that the most probable space groups would be D_{2h}^{10} D_{2h}^{15}, C_{2h}^{5} or C_{2h}^{6} with two or four molecules per unit cell.[22] In view of the crystal space group for other molecules of similar structure either the monoclinic (C_{2h}^{5}) or orthorhombic (D_{2h}^{15}) space groups could be expected to give a close-packed arrangement of molecules retaining C_i symmetry.

A temperature study of the far-infrared spectrum of the solid showed that the 82 cm^{-1} band sharpens drastically with annealing and results from an intermolecular fundamental. The 94 cm^{-1} band was not particularly temperature sensitive so it was concluded that this band was the torsional fundamental which shifted from 54 cm^{-1}. Such a drastic shift with condensation for the torsional oscillation has been found for the glyoxal molecule[18] where the band shifted from 128 cm^{-1} in the gas phase to 192 cm^{-1} in the solid.

Attempts to observe the microwave spectra of glyoxal[23], diacetyl[23], and oxalyl chloride[24] have been unsuccessful. However, the microwave spectrum of oxalyl chloride may be so weak due to quadrupole splitting that its observation would be extremely difficult. Oxalyl fluoride, having only one isotope and no quadrupole moment, should represent a more ideal case; and observation of the microwave spectrum would provide conclusive proof of the existence of a cis isomer.

Acknowledgment

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Table I. Vibrational Frequencies of Solid Oxalyl Fluoride.

Infrared $\nu(cm^{-1})$	Relative Intensity	Raman $\Delta\nu(cm^{-1})$	Relative Intensity	Assignment
3709	w			$\nu_1 + \nu_9 = 3723$
2389	w			$\nu_2 + \nu_{10} = 2412$
2348	vw			$\nu_1 + \nu_6 = 2327$
1962	w			$\nu_2 + \nu_{11} = 1966$; $\nu_1 + \nu_7 = 1960$
1922	w			$\nu_3 + \nu_{10} = 1934$
1897				(residual *cis*)
		1874	m	$\nu_2 + \nu_4 = 1885$
		1866	vs	ν_1
1857	s			ν_9
1842	sh			ternary combinations in Fermi resonance with ν_9.
1825	sh			
1820	m			
1777	vw			(residual *cis*)
1541	vw			$\nu_{10} + \nu_5 = 1542$
		1290	w	ν_2
1274				$\nu_3 + \nu_6 = 1273$
1260				$\nu_{11} + \nu_4 = 1271$ (residual *cis* ?)
1122	vs			ν_{10}
1085	s			$\nu_{11} + \nu_5 = 1096$
1070	sh			$\nu_3 + \nu_{12} = 1077$
		838	w	$2\nu_5 = 840$
		812	s	ν_3 factor group splitting
		799	m	
676	s			ν_{11}

Table I (continued)

Infrared $\nu(cm^{-1})$	Relative Intensity	Raman $\Delta\nu(cm^{-1})$	Relative Intensity	Assignment
		595	vw	ν_4
		513	w	ν_8
		488		glass band
461	s			ν_6
		420	m	ν_5
265	w			ν_{12}
94				ν_7
82				lattice
		57	m	lattice(ghost) ?

Abbreviations: m, medium; s, strong; w, weak; v, very; sh, shoulder.

Table II. Summary of the Fundamental Frequencies for trans-$(COX)_2$ Compounds in the Solid State.

Symmetry Species and Approximate Description of the Normal Vibrations	$(CHO)_2$[a]	$(COCH_3)_2$[b]	$(COF)_2$[c]	$(COCl)_2$[d]	$(COBr)_2$[e]
a_g					
C=O stretch	1729	1719	1866	1762	1752
C-C stretch	1078	1001	812	1093	1052
C-X stretch	2882	693	1290	620	582
COX bend	1364	614	595	427	345
COX rock	551	380	420	287	191
a_u					
COX out-of-plane bend	842	360	461	391	362
COX torsion	192	66	94	55	40
b_g					
COX out-of-plane bend	1050	526	513	444	358
b_u					
C=O stretch	1707	1706	1857	1769	1792
C-X stretch	2890	943,910	1122	756	664
COX bend	1333,1326	544	676	498	405
COX rock	388	265	265	220	176

[a] reference 18

[b] reference 20

[c] this work

[d] reference 9

[e] reference 10

TABLE III. FUNDAMENTAL FREQUENCIES OF trans-OXALYL FLUORIDE

Vibration No.	Symmetry Species and Approximate Description of Normal modes	Raman Solid (cm^{-1})	Infrared Solid (cm^{-1})
	a_g		
ν_1	C=O stretch	1866	
ν_2	C-F stretch	1290	
ν_3	C-C stretch	812	
ν_4	FCO bend	595	
ν_5	FCO rock	420	
	a_u		
ν_6	FCO out-of-plane bend		461
ν_7	torsion		94
	b_g		
ν_8	FCO out-of-plane bend	513	
	b_u		
ν_9	C=O stretch		1857
ν_{10}	C-F stretch		1122
ν_{11}	FCO bend		676
ν_{12}	FCO rock		265

Table IV (continued)

Infrared(cm^{-1})				Raman(Δcm^{-1})		
Gas	Intensity	Solid	Intensity	Liquid	Solid	Assignment
1870 P		1878 sh				
1865 ctr	s	1857	vs			ν_9
1859 R						
		1842 sh				ternary combination in Fermi resonance with ν_9.
1828 sh	w	1825 sh				
		1820 m				
1599 R						
1593 ctr	vw					$2\nu_3$(cis)
1587 P						
		1541	vw			$\nu_{10} + \nu_5$
1509						cis$^{\delta}$
				1384		cis$^{\delta}$
				1278	1290	ν_2
1313 sh	w					
1273 R		1273	vw			
1267 ctr	s	1260	vw			ν_9 (cis)
1261 P						
1218 sh	w					cis$^{\delta}$
1202 sh	w					
1188 sh	w					cis$^{\delta}$
1113	s					
1097	s	1122	vs			ν_{10}
1084 sh		1087	s			$\nu_{11} + \nu_5$
1074 sh		1070 sh				$\nu_3 + \nu_{12}$
				830	838	$2\ \nu_5$
				804	812	ν_3
				799		
805 R						
799 ctr	m					ν_3(cis)
794 P						
		760				
679 R						
673 Q						
668 P		676	s			ν_{11}
664 P						ν_4(cis)

Table IV. Vibrational Spectra of Oxalyl Fluoride in the Fluid and Solid States.

Infrared(cm^{-1})				Raman(Δcm^{-1})		Assignment[+]
Gas	Intensity[*]	Solid	Intensity[*]	Liquid	Solid	
3775 R						
3766 ctr	w					$2\nu_8$, $\nu_1 + \nu_8$(*cis*)
3758 P						
3720 R						
3713 ctr	m	3709	w			$\nu_1 + \nu_9$
3709 P						
3691 sh	w					
3633 R						
3627 ctr	vw					*cis*$^{\delta}$
3621 P						
3554	vw					
3145 sh						$\nu_9 + \nu_8$(*cis*)
3129						
2982 sh	w					
2971						*cis*$^{\delta}$
2963 sh	w					
2926						
2673	vw					$\nu_3 + \nu_8$(*cis*)
2665						
2527	vw					
2363	w	2389				$\nu_2 + \nu_{10}$
2315 R						
2309 ctr	vw					*cis*$^{\delta}$
2304 P						
2150	w					*cis*$^{\delta}$
1950 sh	vw	1962	w			$\nu_2 + \nu_{11}$; $\nu_1 + \nu_7$
		1923	w			$\nu_3 + \nu_{10}$
1897 sh	s	(1897)	vw			ν_8 (*cis*)
				1882	1874	$\nu_2 + \nu_4$
				1867	1866	ν_1

Table IV. (continued)

Infrared(cm^{-1})				Raman(Δcm^{-1})		Assignment
Gas	Intensity	Solid	Intensity	Liquid	Solid	
					595	ν_4
				553		*cis*[δ]
					513	ν_8
510	vw					
500	vw					
				483	488	glass
421	m	461	s			ν_6
				420		ν_5(*cis*)
				415	420	ν_5
264	w	265				ν_{12}
				249		*cis*[δ]
54		94				ν_7
		82				lattice
					57	lattice (ghost)?

---

[*] Abbreviations: s, strong; m, medium; w, weak, v, very; sh, shoulder ; ctr, center.

[+] All bands not indicated as due to the *cis* isomer are due to the trans isomer.

[δ] Believed to arise from *cis* fundamentals or combination bands.

Figure Captions

Fig. 1 - Infrared spectra of oxalyl fluoride; upper curve, solid phase; lower curve, vapor phase.

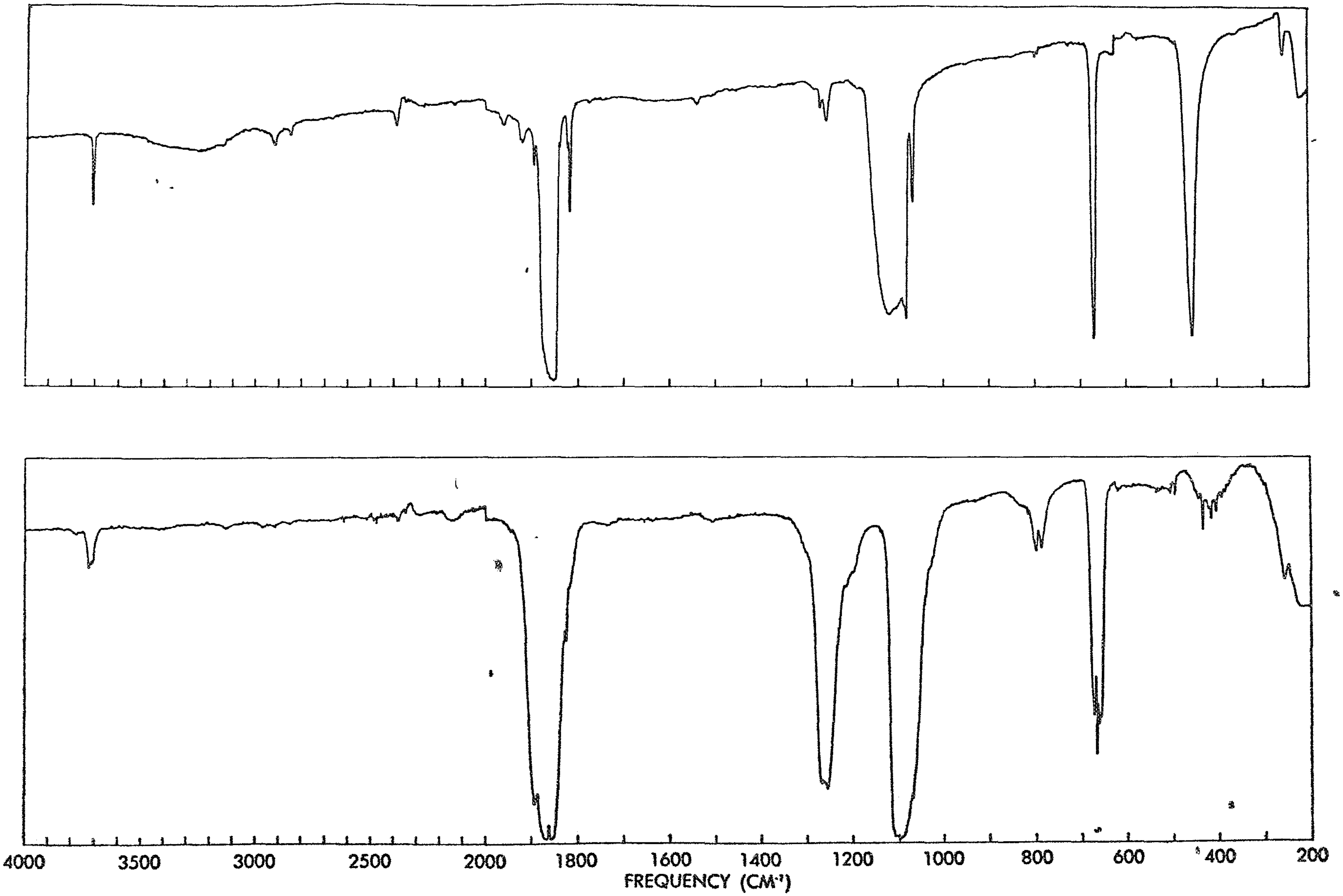
Fig. 2 - Raman spectrum of liquid oxalyl fluoride.

Fig. 3 - Raman spectrum of solid oxalyl fluoride.

Fig. 4 - Steps in the annealing of a solid oxalyl fluoride sample; arrows indicate bands which disappear.

Fig. 5 - Far-infrared spectrum of solid oxalyl fluoride.

Fig. 6 - Far-infrared spectrum of gaseous oxalyl fluoride.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3500
3000
2500
2000
1800
1600
1400
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1000
800
600
400
200
FREQUENCY (CM⁻¹)

Fig. 1

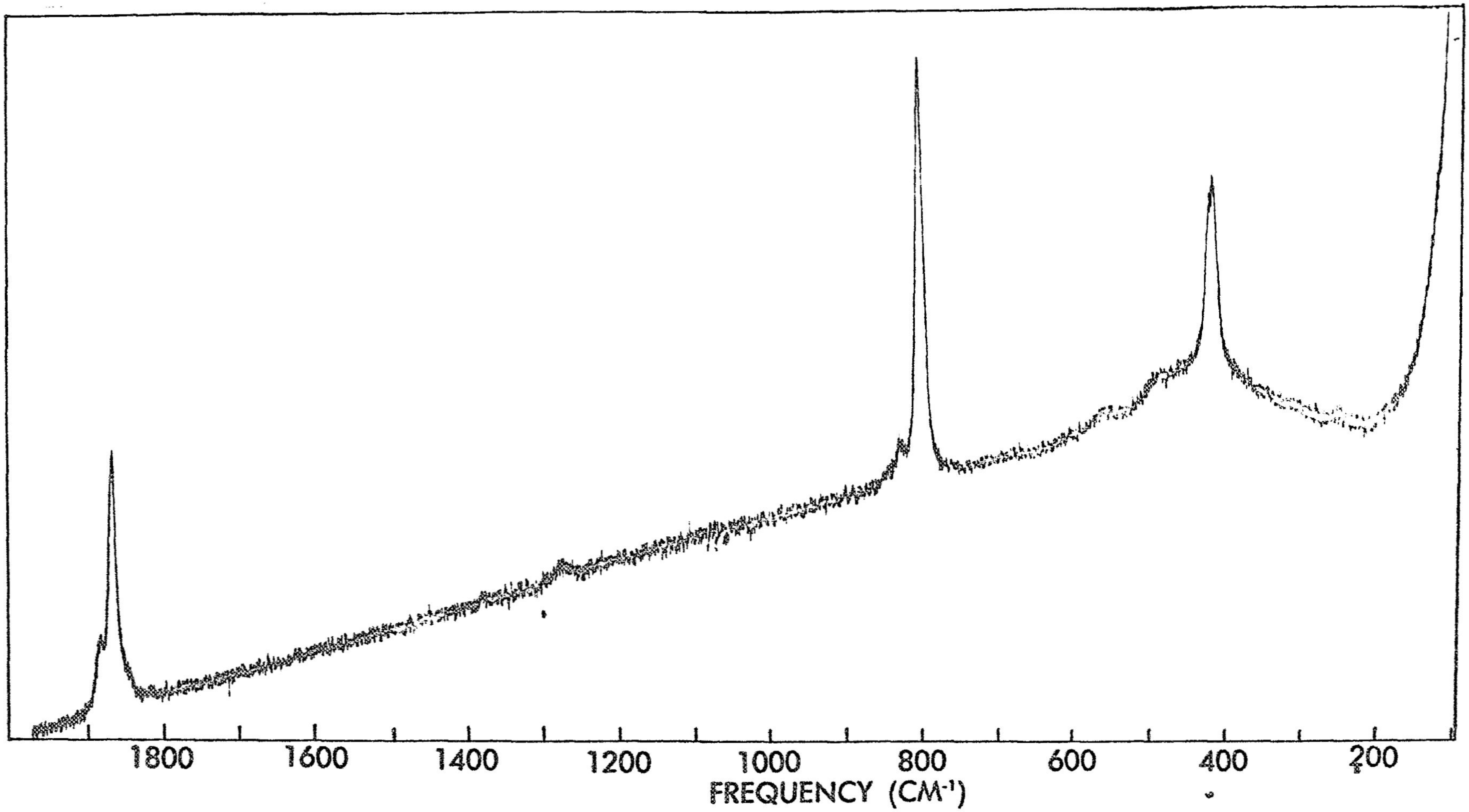

Fig. 2

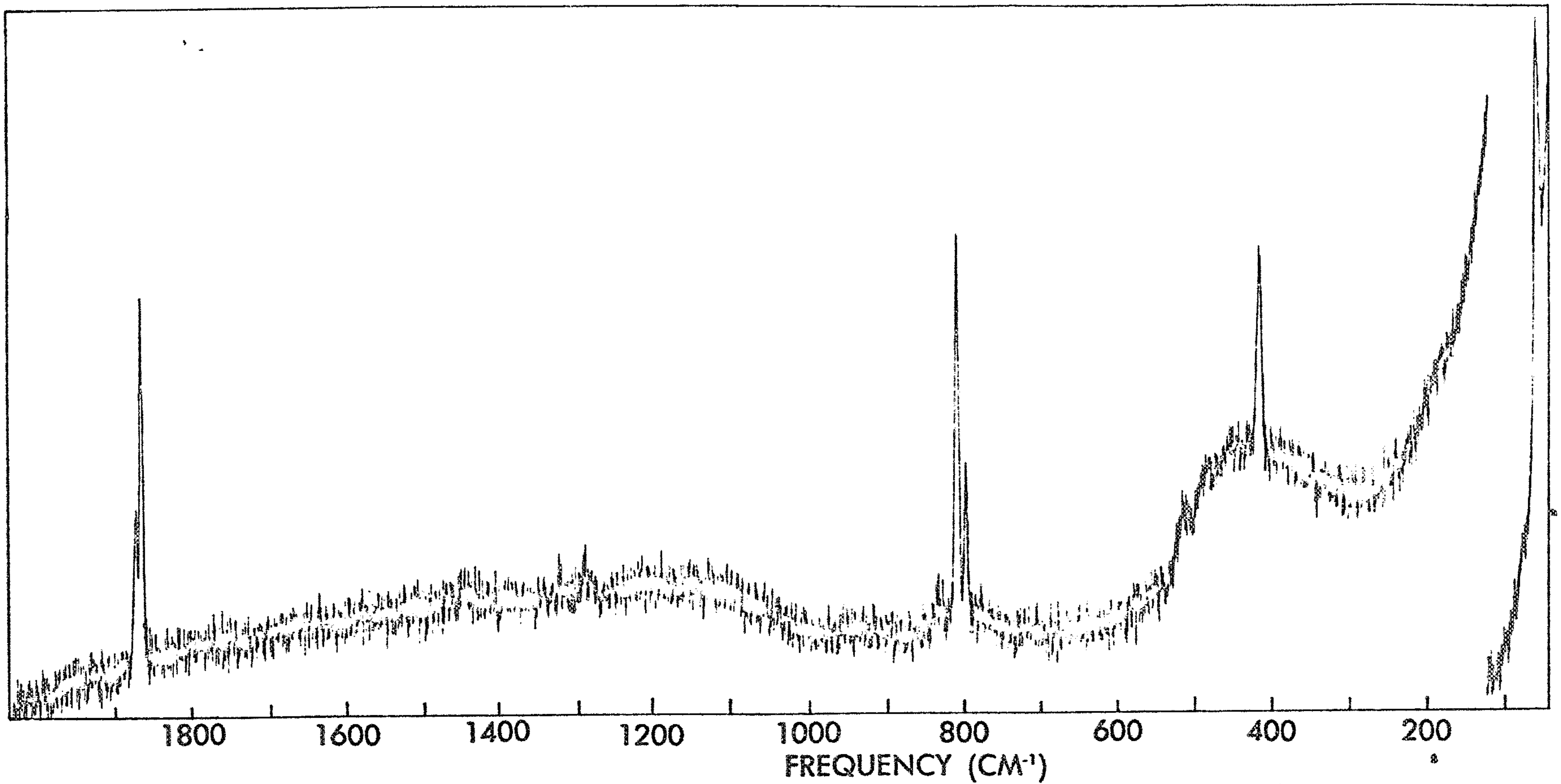

Fig. 3

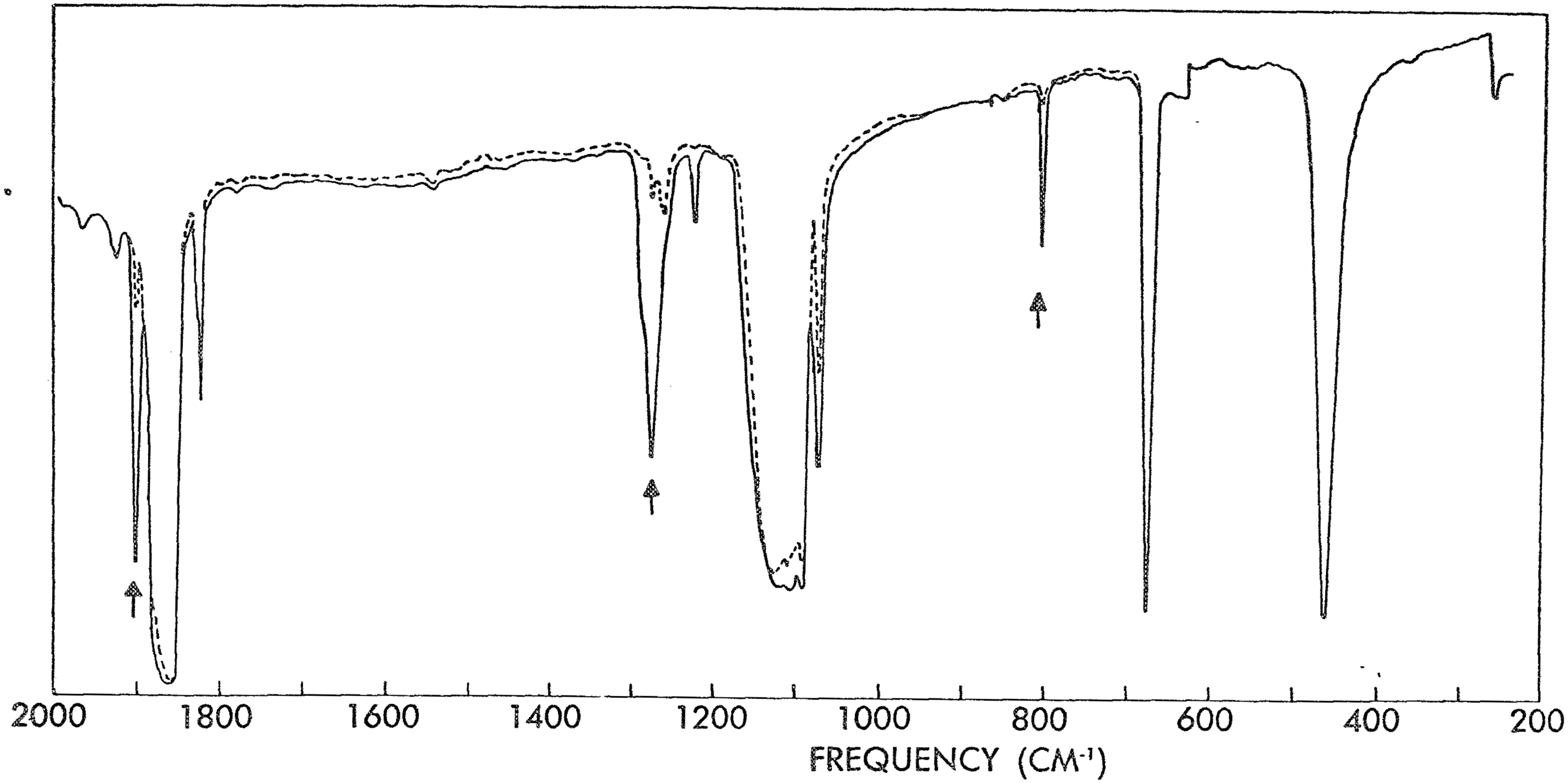

Fig. 4

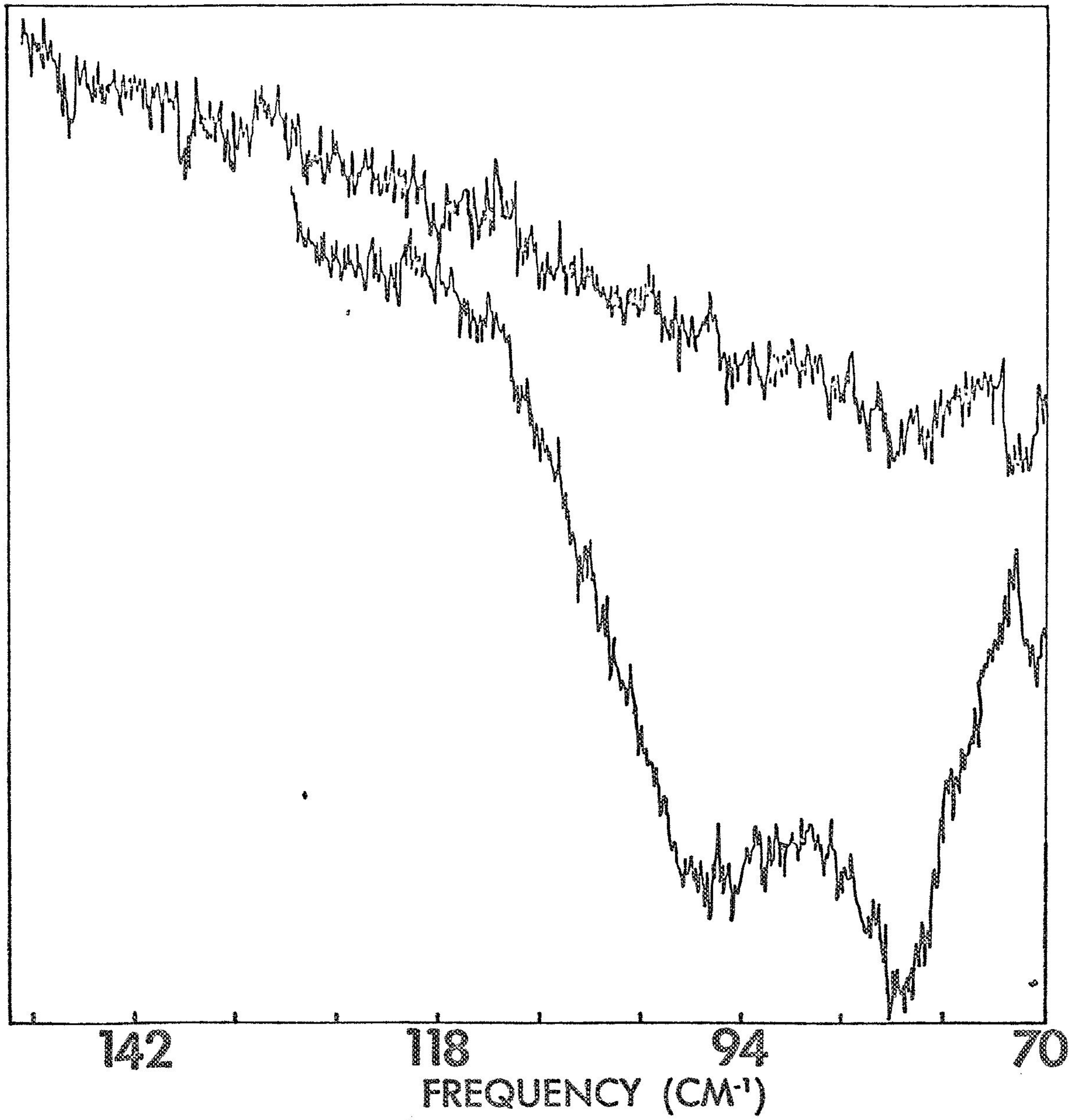

Fig. 5

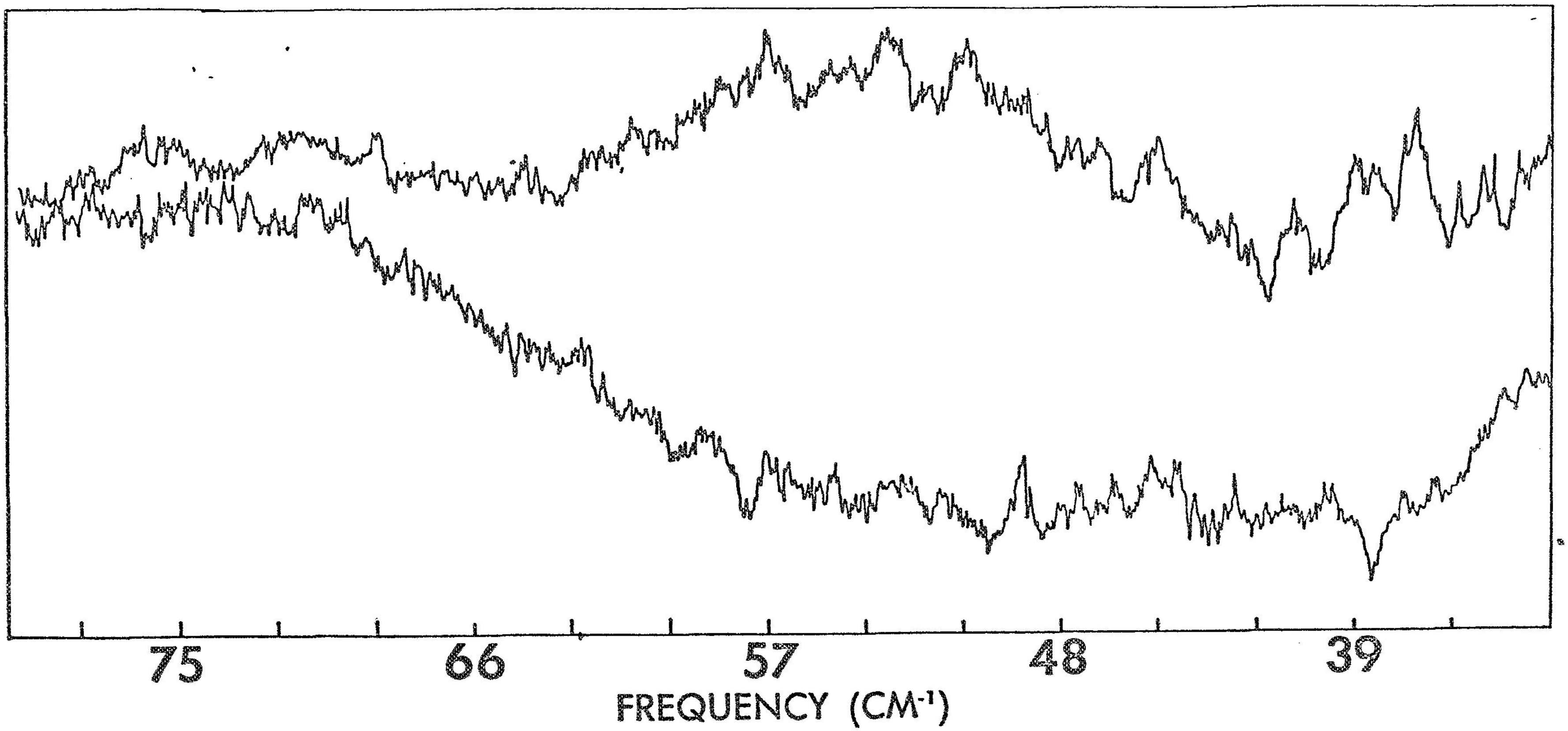

Fig. 6